

DETERMINATION OF MOLECULAR SPECTROSCOPIC PARAMETERS AND
ENERGY-TRANSFER RATES BY DOUBLE-RESONANCE SPECTROSCOPY

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ABSTRACT

The spectroscopy of small to medium-size polyatomic molecules can be extremely complex, especially in higher-lying overtone and combination vibrational levels. The high density of levels also complicates the understanding of inelastic collision processes, which is required to model energy transfer and collision broadening of spectral lines. Both of these problems can be addressed by double-resonance spectroscopy, *i.e.*, time-resolved pump-probe measurements using microwave, infrared, near-infrared, and visible-wavelength sources. Information on excited-state spectroscopy, transition moments, inelastic energy transfer rates and propensity rules, and pressure-broadening parameters may be obtained from such experiments. Examples are given for several species of importance in planetary atmospheres, including ozone, silane, methane, and ammonia.

INTRODUCTION

Research on the properties and dynamics of planetary atmospheres of the outer planets makes extensive use of spectroscopic probes of local atmospheric conditions obtained either from ground-based platforms or remote probes such as the Voyager or Galileo missions. Planetary observations of the spectra of dominant and trace atmospheric constituents in the form of absorption, emission, or reflectance spectra make it possible to

estimate local temperatures, to measure local partial pressures of the species observed, and to estimate the local pressures of other species, but only when supporting data such as spectroscopic assignments, absolute intensities (transition strengths), and sufficiently complete measurements of self- and foreign-gas pressure-broadening energy-transfer processes are available. With the ambitious program of planetary probes planned for the coming decade, there is an urgent need for such data to be provided.

Double-resonance (transient pump-probe) spectroscopy is a powerful technique for providing data of this kind, especially for higher-lying molecular vibrational levels. In this survey, we shall describe the principles of the double-resonance technique (with emphasis on infrared double-resonance [IRDR] spectroscopy), and present some applications to several species of importance in planetary atmosphere research.

PRINCIPLES OF DOUBLE RESONANCE SPECTROSCOPY

Double-resonance spectroscopy may be defined¹ as the use of two resonant one-photon interactions in a single molecule to probe molecular energy levels and relaxation properties. One of the radiation fields, denoted the pump, is a monochromatic, high-intensity field which saturates a pair of energy levels in the system, *i.e.*, transfers a substantial amount of population from the lower level to the (normally unpopulated) upper level. The pump source is typically a high-power infrared or optical-frequency laser. The probe field, which is tuned to another transition in the system, monitors intensity changes correlated with the presence of the pump radiation.

A three-level double-resonance scheme is one in which fields at two different frequencies couple a given molecular energy level to two other levels. The common level may be either lower in energy than the other two, as in Fig. 1(a), or may be higher than the other two, as in Fig. 1(b). Three-level configurations of this

type are often used for *spectrum simplification*; since the number of transitions which are correlated in pairs as shown in Figs. 1(a) and 1(b) is substantially less than the total number of absorption lines, a congested molecular spectrum may be reduced to a much smaller number of lines, and combination differences may be readily identified. The common level may also be intermediate between the lower and upper levels, as shown in Fig. 1(c). In this case, the transition at frequency ν_2 is termed an *excited-state absorption*, and provides information on the fine-structure levels of vibrationally or electronically excited states which are frequently not accessible to ordinary one-photon absorption or emission spectroscopy. If both pump and probe levels are at visible wavelengths, the upper state *a* can often be detected by u.v. fluorescence; this technique is referred to as "optical-optical double resonance"².

In a *four-level* double-resonance scheme, the two radiation fields connect pairs of levels not possessing a level in common, as shown in Figs. 1(d) - 1(f). In order for a double-resonance effect to occur, at least one level in each of the two pairs must be coupled to one of the directly pumped levels by collisional relaxation processes. Four-level double-resonance experiments thus yield information on both the kinetic rates and state-to-state propensity rules for inelastic molecular collisions.

Double-resonance signals may be described by steady-state solutions of the Optical Bloch Equations^{3,4,5}. Indeed, the basic theory for the three-level double-resonance experiment was first developed by Javan⁶ in 1957 for describing the three-level maser. Since the transition moment for the pumped level is a fundamental parameter in the theory, it is often possible to extract information about such moments from quantitative modeling of double-resonance signal shapes and intensities.

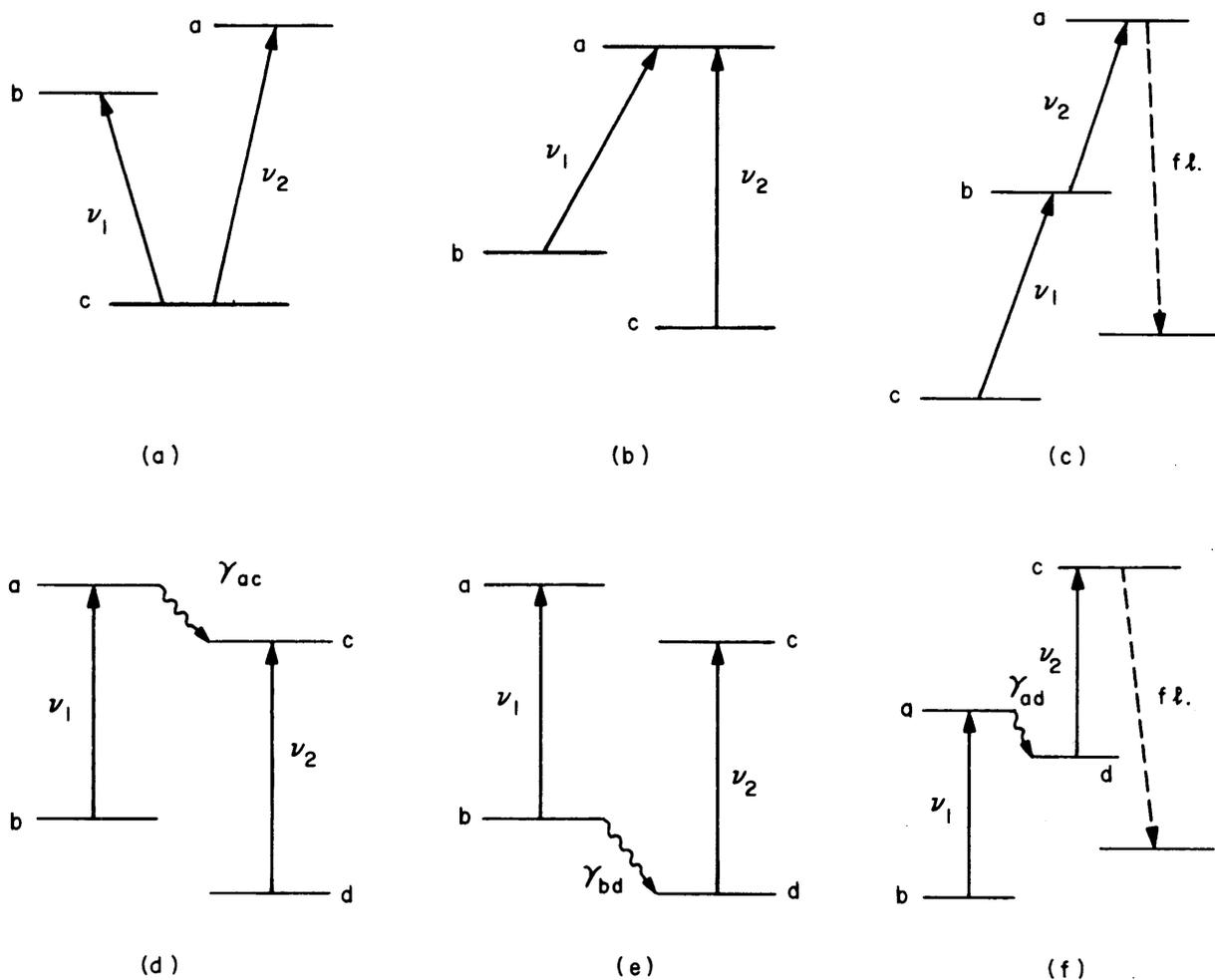


Figure 1. Diagrammatic representations of (a)-(c) three-level double-resonance spectroscopy and (d)-(f) four-level double-resonance spectroscopy [from Ref. 1].

EXPERIMENTAL TECHNIQUES

As noted above, the pump field in a double-resonance scheme must be capable of saturating the transition with which it is in resonance. This implies two requirements on the experiment: first, the population of the upper pumped level should be substantially less than that of the lower level, so that transfer of population from the lower to the upper level will be reflected in changes in transmitted probe radiation intensity. Second, the pump source must have sufficient intensity to at least partially saturate its transition. The first criterion would suggest a limitation to pumping vibrationally or electronically excited levels; however, because of the sensitivity of phase-sensitive microwave detection,

microwave-microwave double-resonance has been applied with great success to the study of collisional relaxation among rotational levels^{1,7}.

The development of tunable, high-power infrared and visible-wavelength lasers has made it possible to extend the double-resonance technique to vibrationally and electronically excited states. In particular, the pulsed CO₂ laser, which is line-tunable in the 9 - 11 micron region, has been used in many experimental investigations, including those in our laboratory. At high IR laser fluences ($> 1 \text{ J cm}^{-2}$), these lasers can induce molecular dissociation or isomerization via infrared multiple-photon excitation processes^{8,9,10}; double-resonance pump-probe experiments have been a valuable technique for characterizing the level distributions produced in IRMPE processes.

The essential requirements on the probe radiation in a double-resonance experiment are those of frequency and amplitude stability. Microwave klystrons, c.w. dye lasers, and tunable semiconductor diode lasers have all been used as double-resonance absorption probes¹; when fluorescence excitation/emission spectroscopy can be used, its high sensitivity, energy resolution, and time resolution make it an excellent probe choice. A large proportion of the experiments in our laboratory are based on diode-infrared laser-double resonance spectroscopy (IRDR)¹¹, and the results to be discussed in the following section have been obtained primarily using this technique.

To avoid some of the limitations of absorption or fluorescence excitation spectroscopy, several other spectroscopic techniques have been applied to double-resonance experiments. Raman spectroscopy, for example, is applicable to all molecules, is state-specific, and affords good time resolution when a pulsed laser is used as the Raman probe source. Its major and obvious disadvantage is the extremely small magnitude of the spontaneous Raman scattering cross section, which severely limits the sensitivity. This problem can be alleviated by using resonance-

enhanced or coherent Raman scattering, such as Coherent Anti-Stokes Raman (CARS); the nonlinearity inherent in such techniques, however, make interpretation of the data quite difficult. Resonant multiphoton ionization (REMPI) is another promising probe technique; a CO₂-laser-pump/REMPI-probe experiment on ammonia has recently been carried out by Shultz and co-workers¹², in which the formation and decay of $v_2 = 1^-$ levels could be monitored.

APPLICATIONS TO ATMOSPHERIC SPECIES

The primary objective of our IRDR investigations of small polyatomic molecules has been the determination of energy transfer rates and pathways in these systems, and subsequent comparison with collision models. The experiments also provide information on spectroscopic parameters for vibrationally excited states, transition moments, and pressure-broadening coefficients. In this section, we briefly summarize some key results of these investigations, and suggest directions for future work.

Methane

Methane is both a trace constituent of the terrestrial atmosphere, where it may contribute to global temperature change via the "greenhouse effect"¹³, and a major constituent of the atmospheres of the outer planets and their satellites. While the vibration-rotation spectroscopy of methane and other spherical tops has been analyzed in great detail by several research groups, there was a paucity of data, both qualitative and quantitative, on state-to-state energy transfer in such molecules. Microwave double-resonance spectroscopy⁷ is not generally applicable to such molecules, due to the absence of a permanent dipole moment. Laser-excited infrared fluorescence, which is very useful for elucidating vibrational relaxation pathways in polyatomic molecules, does not have sufficient resolution to probe the rotational fine structure. Other techniques for studying relaxation

processes, such as ultrasonic dispersion, thermal lensing, and photoacoustic spectroscopy, are essentially bulk rather than state-resolved measurements.

Our IRDR studies on methane¹⁴ represented the first measurement of state-to-state rotational energy transfer in a spherical top molecule. To obtain a good coincidence between a methane absorption line and a CO₂ laser pump line, we had to use the doubly labeled isotope ¹³CD₄; however, the results obtained are applicable to the normal CH₄ isotope and to other spherical tops such as silane (following section). The overall relaxation rates are approximately equal to the Lennard-Jones collision rate and are nearly independent of collision partner, as might be expected for collisions taking place via a short-range intermolecular potential. By applying a kinetic Master-Equation analysis, we were able to represent the rotationally inelastic collision rates by an exponential energy-gap law:

$$k_{fi} = (2J_f + 1) k_o \exp\{-C(E_i - E_f)/k_B T\} \quad (1)$$

with the scaling parameter $C = 0.8$; this permits rotationally inelastic collisions with J changes of up to ± 5 , which is also consistent with the action of short-range, impulsive forces.

The surprises were found in the final-state specificity of the rotationally inelastic collisions, which reveal a dramatic selectivity of rotational energy transfer pathways with respect to rotational fine-structure states. The first point noted was that molecules tend to remain within the initially pumped Coriolis sublevel of the $v_4 = 1$ state; this can be expressed as a propensity rule for conserving the vibrational angular momentum $R - J$ in the collision. In addition, rotational relaxation appears to proceed via "principal pathways", which constitute a small subset of the energetically accessible levels. The nature of these pathways was clarified by subsequent experiments on silane, which we now consider.

Silane

Although silane has not been identified as a major component of planetary atmospheres, experiments on this system provide considerable insight into rotational energy transfer mechanisms discerned in the earlier experiments on methane, and suggest important connections between these measurements and pressure-broadening phenomena. In addition, silane is widely used for preparation of electronic materials by thermal and laser-assisted chemical vapor deposition¹⁵, so the study of laser-pumping mechanisms and collisional relaxation in this system has considerable practical importance.

The SiH_4 infrared absorption lines which lie nearest to the 10P(20) CO_2 laser line are the A_2 , F_2 , and E components of the $J = 13 \leftarrow J = 12$, $v_4 = 1 \leftarrow 0$ band. These are detuned from the laser frequency by 1015, 600, and 378 MHz, respectively. As a result of these detunings, IRMPE of silane can occur only under pressure-broadened¹⁶ or laser-induced breakdown conditions¹⁷. The $v_4 = 1 \leftarrow 0$ transition moment is sufficiently large, however¹⁸, that the pulsed TEA CO_2 laser can pump a considerable fraction of the population of each of these symmetry levels into the excited rovibrational state¹⁹, which can then be followed by diode absorption at appropriate hot-band transitions.

Both rotational²⁰ and vibrational²¹ relaxation have been measured in silane using IRDR. V-V energy transfer between $v_4 = 1$ and $v_2 = 1$ levels is nearly as efficient as pure rotational energy transfer, as a result of the strong Coriolis mixing between these two states. The scaling coefficient C in Eq. (1) for rotationally inelastic collisions is 0.05 - 0.08 for the three symmetry species; when the larger rotational level spacing of silane in $J = 13$, as compared with $^{13}\text{CD}_4$ in $J = 11$, is taken into account, this corresponds to a somewhat slower fall-off of inelastic collision probability with increasing ΔJ . The **R - J** conserving propensity rule found in methane is validated for all three symmetry species

in silane; in addition, the pattern of "preferred pathways" for rotational state changing collisions now shows an interesting regularity²². Rotational states of spherical tops, such as methane and silane, are split into numerous fine-structure components by centrifugal and anharmonic interactions; these components arrange themselves in level clusters according to whether the rotation is quantized along the 6-fold or the 8-fold symmetry axis of the molecule. The preferred pathways for all three symmetry species of a given rotational state always lie as close to each other as possible in the cluster structure, and these generally correspond to the same quantization as that for the initially pumped level. One way to summarize the selectivity found for rotationally inelastic collisions is that a "conservation of coupling" propensity rule is at work.

The ability to interrogate all three nuclear-spin symmetry species of silane has led to an observation with important implications for understanding pressure-broadening coefficients, which are essential for atmospheric remote sensing methods. The total rotational relaxation rates for these symmetry species show significant differences at the 95% confidence level²⁰, with the ordering $k(F_2) > k(A_2) > k(E)$. This is the same ordering as has been found for the infrared absorption pressure-broadening coefficients for methane^{23,24}, as well as in recent measurements by the Dijon group²⁵ of pressure broadening in the Q branch of the ν_1 Raman band of $^{13}\text{CD}_4$. Furthermore, the ratio of the symmetry-averaged Raman-broadening coefficients for silane²⁵ to that of $^{13}\text{CD}_4$ ($R = 1.24$) is very close to the correspondingly averaged IRDR relaxation times ($R' = 1.28$). The direct measurements thus provide details of the inelastic collision rates which are averaged out in the usual experimental and theoretical treatments of pressure broadening, and can serve as stringent tests of the theories. In the following section, we describe the application of this approach to ozone, for which a major effort in determining accurate pressure broadening parameters is now under way.

Ozone

The role of ozone in stratospheric photochemistry and in the radiative properties of the upper atmosphere is too well known to elaborate upon here. Although a large data base exists with respect to the spectroscopic and kinetic properties of this molecule, a recent survey²⁶ identified a nearly total lack of data for rotational energy transfer in ozone collisions. Without such data, current theories for pressure broadening can receive only limited testing.

The IRDR technique is admirably suited for the measurement of these data. In earlier u.v. absorption - infrared laser double resonance experiments, we had identified coincidences of ozone absorption features with CO₂ laser lines, and made use of the u.v. spectral changes following vibrational excitation to determine Hartley band absorption in the vibrational excited state²⁷ and to map out part of the vibrational relaxation pathways for this molecule²⁸. Using the IRDR technique, we are able to follow these processes at the rotational state-to-state level.

The IRDR scheme for the CO₂ 9P(12) laser line is shown in Fig. 2. This line pumps the $17_{4,13} \leftarrow 16_{4,12}, v_3 = 1 \leftarrow v_3 = 0$ transition. Relaxation into the depleted $J = 16$ level can be monitored by the three-level IRDR transition at 1026.51 cm^{-1} , and relaxation out of the $J = 17, v_3 = 1$ level by the hot-band transition at 1028.58 cm^{-1} . By monitoring four-level IRDR signals at other frequencies, some of which are shown in Fig. 2, the propensity rules governing rotationally inelastic collisions can be determined. Additional measurements of hot-band transitions originating in the $v_1 = 1$ level will permit us to measure the V-V rate between the $v_3 = 1$ and $v_1 = 1$ levels, which could not be resolved in the earlier u.v./IR double resonance experiments²⁸.

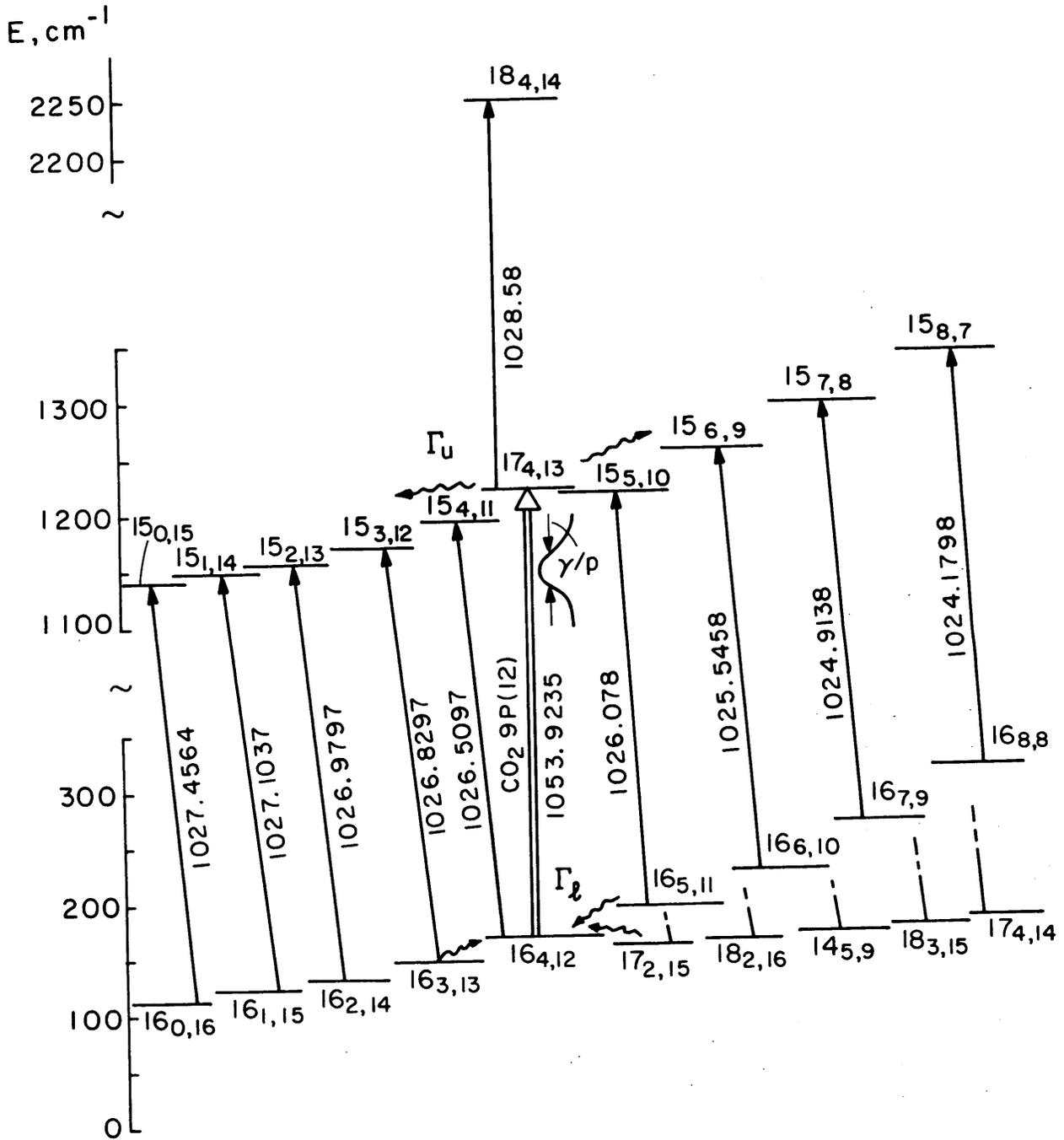


Figure 2. Infrared double-resonance level scheme for CO₂ laser 9P(12) pumping of ozone, showing probe frequencies for three- and four-level IRDR configurations.

CONCLUSIONS AND FUTURE PROSPECTS

The examples described in this report illustrate the power of the double-resonance technique in determining energy transfer

rates and pathways, in both the ground and vibrationally excited states of polyatomic molecules. The resulting data base can then be employed to test inelastic scattering theories and assess intermolecular potential models, both of which are necessary for the systematization and prediction of infrared pressure-broadening coefficients, which are in turn required by infrared remote sensing techniques for both terrestrial and planetary atmospheres. In addition, accurate measurements on excited-state absorption transitions permits us to improve the determination of rotational and vibrational spectroscopic parameters for excited vibrational levels, and to derive band strengths for hot-band transitions involving such levels.

Further development of this technique will make use of pulsed visible and near-infrared laser sources to pump vibrational overtone levels, which can then be interrogated by tunable infrared diode laser absorption. As an example, consider the overtone spectrum of normal methane, CH_4 . The spectrum is particularly difficult to rotationally assign because the spectral congestion caused by Fermi resonance interactions increases dramatically with the number of H atoms. While CHD_3 has a resolved and assignable room temperature spectrum in the 5 C--H quanta region, the CH_4 spectrum is essentially unresolved at this temperature. When cooled to temperatures characteristic of planetary atmospheres (40 - 200 K), however, the spectrum resolves into Doppler-limited features²⁹. The identification of these features will be greatly facilitated by the spectrum simplification afforded by double-resonance spectroscopy. Further information on relaxation out of these highly excited vibrational levels will be enormously interesting for comparison with current theories of molecular dynamics³⁰, as well as for developing models for pressure broadening in overtone absorption spectra.

ACKNOWLEDGMENTS

The development and previous applications of the double-resonance technique in our laboratory have been supported by the National Science Foundation and the Air Force Office of Scientific Research. The current research on inelastic collision processes in ozone is supported by NASA Upper Atmosphere Research Program Grant NAGW-1667.

References and Notes

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